

REPORT

RESEARCH GRANT NAG 1 1836

**Testing and Further Development of Improved Etches and Etching Methods
for the Analysis of Bridgman Grown Semiconductor Crystals with an
Emphasis on Lead-Tin-Telluride**

**Patrick G. Barber
Professor of Chemistry
Longwood College, Farmville, Virginia 23909**

31 March 1998

Abstract

The goals outlined for the research project for this year have been completed, and the following supporting documentation is attached:

1. A copy of the proposal outlining the principal goals:
 - a. Improve the characterization of semiconductor crystals through new etches and etching procedures.
 - b. Developed a novel voltammetric method to characterize semiconductor crystals as a result of searching for improved etches for lead-tin-telluride.
 - c. Presented paper at ACCG-10.
 - d. Prepared manuscripts for publication. Completed additional testing suggested by reviewers and re-submitted manuscripts.
 - e. Worked with an undergraduate student on this project to provide her an opportunity to have a significant research experience prior to graduation.
2. In addition to the anticipated goals the following were also accomplished:
 - a. Submitted the newly developed procedures for consideration as a patent or a NASA Tech Brief.
 - b. Submitted a paper for presentation at the forthcoming ICCG-12 conference.
3. A copy of the final draft of the publication as submitted to the editors of the Journal of Crystal Growth.

New and Improved Etches for lead-tin-telluride-- voltammetric analysis

To improve the results obtained by etching the cut and freshly polished faces of lead-tin-telluride samples grown using a Bridgman furnace, the existing Norr etch was improved by finding a dilute concentration that when coupled with electroetching revealed the desired surface features without also developing an obscuring deposit. This modified procedure was used successfully on samples grown in the normal gravity of earth. This improvement gave qualitative results on semiconductor crystal quality, but quantitative results were not going to be easily obtained and automation of the procedure was not possible.

In the process of developing the improved protocol for use in electroetching, a new method was

developed by adapting the traditional differential pulsed stripping voltammetry. This method is described more fully in the attached paper. It involves immersing the semiconductor face in the etchant and following the progress of the etching process using a glassy carbon working electrode. Because this method is so sensitive, it was necessary to also develop new etchants that are only millimolar in concentration. The most successful one involved a bromine/bromide etchant, which is described in the attached paper. The semiconductor is attacked and ions from it are dissolved in the etchant. During the deposition cycle of the voltammetric analysis these ions are concentrated by being deposited for 10 seconds onto the glassy carbon working electrode. When the polarity is reversed, these ions are re-oxidized and redissolve back into the supporting electrolyte which surrounds the electrode. As these ions redissolve, they generate a current which is measured. The more lead has been removed from the surface of the semiconductor crystal, the greater will be this current. This analysis can be repeated every 30 seconds and can follow the etching process. From an analysis of the data versus time it is possible to distinguish different semiconductor samples of lead-tin-telluride on the basis of how quickly the etchant begins to attack the semiconductor crystal, the rate of that attack, and the extent of attack. As summarized in the attached paper, the four samples of lead-tin-telluride behaved differently and in a way that was in agreement with the anticipated crystal quality.

The results of these voltammetric conclusions were verified through subsequent etching using the improved Norr electroetch procedure. The dislocation pit densities on the surfaces of the crystals were counted using the traditional optical microscopic method, and these densities were also in agreement with the general trends among the four semiconductor samples tested.

To be a general method of rapid and automated analysis of semiconductor crystals, this voltammetric method needs to be further tested on other samples of lead-tin-telluride and on other semiconductors. It may be economically important as a technique to rapidly to ascertain semiconductor quality.

New and Improved Etches for lead-tin-telluride-- diammine silver ion

Another dilute etch was developed as part of the effort to find etches for lead-tin-telluride that did

not also deposit obscuring films. Diammine silver(I) ion proved to also be successful. This was developed and tested with the help of an undergraduate student, Ms. Carrie Hayes. This project greatly enhanced her educational experience by providing her a chance to engage in significant research before graduation. She is now employed by Lipton Foods in Baltimore, Maryland.

In the procedure developed a very dilute solution of diammine silver(I) ion was used as the etchant in the revised electroetching procedure developed for this project. The electrochemical conditions of voltage, current, and time were kept constant; but the concentration of the reagent was gradually decreased from 50mM to 10mM. After each etching, the semiconductor crystal face was viewed in an optical microscope. The better quality semiconductor crystals required stronger etchant concentrations before surface features such as etch pits were revealed than did the poorer quality semiconductor crystals. Although this method was successful in qualitatively ordering the four lead-tin-telluride samples, it was not easily made quantitative nor did it lend itself to eventual automation. As a consequence, this technique was put aside in favor of the differential pulse stripping voltammetric procedure described above. The details of this diammine silver(I) technique are described in the attached paper.

Submission of a Proposal for a Patent and NASA Tech Brief

The differential pulse stripping voltammetric procedure has been submitted to NASA as a possible patent and NASA Tech Brief.

Publications

A poster and report were prepared on the undergraduate research project. The poster was presented in April 1997 as part of the undergraduate research conference held at the University of Virginia in Charlottesville. "Rapid Method for Estimation of Dislocation Densities in Semiconductors" by Carrie Hayes and Pat Barber.

The poster and paper were presented at the Tenth American Conference on Crystal Growth, ACCG-10 held in Vail, Colorado, in June 1996. After review by the editors of the Journal of Crystal Growth, it was decided to follow their suggestions and include a section comparing the results

obtained with the more traditional method of analysis using optical microscopy.

This additional research was completed during a six week period in the summer of 1997. The paper was revised in accord with the suggestions of the reviewers and resubmitted as part of the proceeding of the ICCG-12 meeting to be held in July 1998. This paper has been accepted for presentation at that meeting and the final manuscript has been submitted to the editors before the deadline. The proceedings should be published before the end of 1998 or very early in 1999. A copy of the final draft of the revised paper is attached to this report.

Transfer of Technology to NASA

Through several trips to the NASA Langley Research Center in Hampton, Virginia, the technologies developed under this research project have been transferred to others who can benefit from the improved methods. These trips occurred mainly during the summers of 1996 and 1997. The techniques were used on earth-grown samples of lead-tin-telluride to perfect them before eventual application to space grown samples.

Further Research Possible

The electrochemical etch procedures and reagents have been developed and tested using a limited number of lead-tin-telluride samples. The same samples have been used to test the voltammetric analytical method. Before these improvements can be said to be of general utility, it is necessary to test them on further samples of the compound semiconductor lead-tin-telluride and on other semiconductors. As the composition of each semiconductor is changed, it is necessary to review the thermodynamics of the electrochemical processes and select the best etchant for each material. Best results seems to be obtained when dilute etchant solutions are used because they tend not to leave obscuring film deposits on the semiconductor surfaces.

A Copy of the Paper "Estimating Crystal Quality in Semiconductors Using Voltammetry" by P. Barber, C. Hayes, N. Baker, and W. Rosch is attached.

**DEVELOPMENT OF IMPROVED ETCHES AND ETCHING
METHODS
FOR THE ANALYSIS OF BRIDGMAN GROWN SEMICONDUCTOR
CRYSTALS
WITH
AN EMPHASIS ON LEAD TIN TELLURIDE**

**Patrick G. Barber
Professor of Chemistry
Longwood College, Farmville, Virginia 23909**

January 19, 1996

Abstract

The ability to visualize semiconductor crystallization in real-time and in-situ has been developed at NASA's Research Centers. Using the radiographic technology developed at the Langley Research Center, crystal growers can observe and adjust experimental variables during actual growth. Even with this capability, there remains the task of determining the quality of the semiconductor crystals. This project will address the need to assess the quality of semiconductor crystals and to correlate these properties with the experimental growth conditions. This project will develop and improve the *etches and etching techniques* that reveal the composition and crystal quality of doped semiconductors. Thermodynamic tables and calculations will be used to understand the etching process and to aid in developing the improved etches. Electrochemical and photochemical methods will be further explored to find improvements in etching techniques.

Presentations to scientific forums such as the American Association for Crystal Growth Conference in August, ACCG-10, and *publications* in scientific journals such as the **Journal of Crystal Growth** will be made to disseminate the technology developed under this grant. The developed analytical technology will be applied to improving furnace and ampoule designs, reducing experimental turnaround time, maximizing the benefits of each experimental run, and improving the quality and quantity of data available from experiments both on earth and in space.

1. Introduction:

1.1. Semiconductor Melt-Solid Interface:

The ability to produce semiconductor crystals of suitable composition and purity in preferred crystal growth orientations is essential for the commercial success of the modern electronics and communications industries. These materials are needed for defense equipment and for consumer products that are a significant part of the nation's economic health.

So important is this ability to produce these materials that they are being studied in the normal gravity of earth and in the microgravity of space. Experiments in crystal growth have flown on U.S. space missions in Spacelabs, Shuttle missions, and are being planned for Space Station. The Europeans have flown crystal growth experiments on sounding rocket flights such as the TEXUS project and on the D-1 mission on Space Shuttle. The Japanese also are involved in developing an extensive crystal growth experimental program for space. The Russian space effort also has placed a high priority on crystal growth experiments during manned flights and onboard the MIR Space Station.

As a part of another project, NASA developed the capability to visualize the melt-solid interface in real-time inside crystal growth furnaces such as those used in Bridgman growth of metals and semiconductors. Crystal growers can now interact with their experiments, and this has resulted in improved capabilities to record the melt-solid interface position and shape, to determine the actual crystal growth rate in situ, in real time, to better appreciate the thermal effects caused by

furnace components such as thermocouples, to facilitate improved ampoule and furnace designs, and to provide remote sensing capabilities enabling scientists to conduct these crystal growth experiments with a minimum of hands-on requirements. The technology now provides the ability to conduct crystal growth experiments efficiently in remote sites including the microgravity of space with scientists and engineers working in ground stations and requiring a minimum of astronaut time and attention. The improved crystal growth data already obtained in test systems using the elemental semiconductor germanium and the compound semiconductor lead tin telluride have proven the utility and value of this technology to the ground-based crystal growth community.

With all of this increased ability to adjust experimental growth conditions there is still the need to know how experimental conditions influence the quality of the resulting crystals. Improved methods to analyze the resulting crystals must be developed, and this proposal will find methods to address these needs.

1.2. Development and Testing of Etchants

Because theories suggest that the crystal interface shape during growth affects the quality of the resulting crystal, there is a need to characterize more fully the products of semiconductor crystal growth to better understand the growth process itself, to better control experimental variables to improve the value and utility of the resulting products, and to facilitate the design of crystal growth furnaces and ampoules. This proposal seeks to improve the characterization of

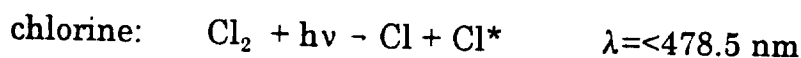
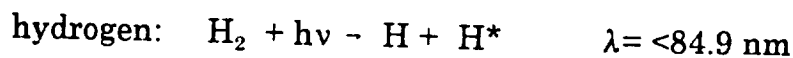
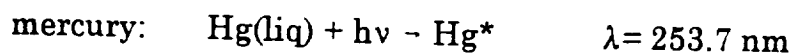
crystals by gathering chemical and electrochemical etchants reported in the literature, cataloging them, testing them, developing new or improved etchants and procedures where needed, and transferring this technology to the personnel at NASA Langley Research Center.

Success has been reported in the literature for etchants such as that developed by Norr for use on Lead Tin Telluride. As reported this chemical etch is so strong that while it dissolves the surface layer, it also obscures it by depositing back a layer of precipitate that forms spontaneously in solution. Earlier work in this area by the principal investigator discovered the thermodynamic reasons for these phenomena. By reducing the chemical strength and augmenting it with an electrochemical procedure, successful etches were developed. This project will search for additional etchants and electrochemical conditions that produce an improved etch of semiconductor crystals.

Preliminary work indicates that similar success in finding better etches may be possible by augmenting dilute chemical etches with photochemical reactions. In this procedure photochemical reactions initiate the etching process by producing transient intermediates that attack the surface of semiconductor crystals. The photochemical reactions replace the electrochemical ones found to be effective in the earlier work. In this process the etchant will contain a photochemically active chemical that will react with the incident light to produce a chemically very active intermediate that will actually etch the semiconductor surface. There are many different photoactive molecules that can be used. Some of these produce reactive

species through excitation, fluorescence, internal conversion, and phosphorescence.

Examples of such photoreactive species include the following:



Other potential reagents include reagents such as luminol, iodine, and other excimers. Some exciplexes formed with the semiconductor may form an alternative route to photochemical etches for these materials.

This project will develop and test etchants and procedures for the analysis of the quality of semiconductor crystals. Thermodynamic, electrochemical, and photochemical data will be used to identify the most likely materials, and electrochemical and photochemical reactions will be used to enhance the etching process.

1.3 Report on the Development of Improved Crystal Analysis Technology:

To provide a summary of the development of this improved crystal analysis technology, reports to NASA Headquarters and other NASA centers such as LaRC and MSFC will be prepared. Analytical methods developed under this grant may find applicability to other crystal systems including HgCdTe and other semiconductors.

1.4 Preparation of Journal Reports:

The significant technology developed to assess crystal quality will be disseminated through journal publications and presentations at scientific meetings. One presentation at the ACCG-10 meeting in August 1996 and one publication in the **Journal of Crystal Growth** are proposed for 1996.

2. Justification of Budget Items:

The budget for this proposal is attached, and a detailed description of the major items and how they relate to the work tasks is given below.

2.1. Personnel:

The salary for the principal investigator is included for three months during the summer of 1996. Part of this time will be spent at the NASA Langley Research Center in Hampton, Virginia, while the rest of the time will be spent at Longwood College in Farmville, Virginia. To prepare samples for analysis, actual crystal growth runs and image enhancements will be done at the Langley facility, since the needed equipment is already in place at that Center and it is not cost effective to duplicate this equipment at another site. The writing of the papers and reports is best done at the college. The gathering of existing etchant procedures, cataloging, testing, and developing improved etchants and etching procedures for observing variations in composition and structure are best done while working in the library and laboratories at Longwood College. The transfer of these improved

techniques to the personnel at Langley must be done at NASA LaRC.

Two undergraduate students will be employed on the project to increase the number of experimental runs that can be made for the new etches and techniques being developed. The funds will be expended nominally during the summer of 1996, but it may increase the availability of students, especially those who must work full-time in the summer to support their studies, if they work on this project during the academic year. This schedule will also free the principal investigator to devote the summer to transferring the technology developed to NASA.

2.2. Publication Costs:

The necessary reports and journal publications must be typed and the presentation materials for the ACCG-10 meetings must be prepared. Tables, graphs, and presentation viewgraphs and posters will also need to be prepared. It is estimated that this will require approximately eighty hours. Journal page charges for papers published by the Journal of Crystal Growth or a similar journal have been included.

2.3. Travel Costs:

To disseminate the results of this improved technology, the results are to be presented at appropriate scientific meetings. It is proposed that this be done at least at the American Conference of Crystal Growth National Meeting to be held in Colorado in August 1996. This meeting is held only once every three years and is

the principal meeting for American crystal growers. Presentation at this important meeting will facilitate the dissemination of this improved analytical technology and will facilitate cooperation in crystal growth projects. The estimated costs for registration, ground transportation, room and board are listed in the proposed budget.

Since some of the proposed work-tasks can only be completed using the facilities available at NASA Langley Research Center, the estimated expenses for travel to NASA-La are listed.

2.4. Supplies:

The costs for consumable paper, chemicals, glass, photographic film, cutting and polishing materials, and plastic supplies are shown on the proposed budget. Since the work tasks involve testing and development of improved etchants and electrochemical etching procedures, some chemicals and glassware are needed for the proposed project.

Some equipment needed for the successful completion of this project has already been purchased by the college. There are some expenses associated with the maintenance of this equipment including microscope cleaning and servicing and supplies to maintain and use the optical, electrochemical, polishing, and computer equipment needed for this project.

2.5. Equipment:

For the successful completion of the work tasks, the following equipment is requested:

Item #1: Peristaltic Pump

The only way in which the etchants have been caused to flow over the semiconductor crystal during electrochemical etching in tests done to date at Longwood College has been to place the sample in a beaker with a stirring bar. This method has worked; but since the fluid flow is irregular, spurious lines are developed in the etch pattern. A more uniform and controllable fluid flow is needed to eliminate these effects. The requested peristaltic pump is an inexpensive method to provide more uniform flow of etchant during the electrochemical etching process.

Item #2: polishing wheel

One wheel is available for use on this project at Longwood College, but it became apparent from previous work that significant time is lost through changing wheels and cleaning polishing pads from one polishing grit to another. It would greatly speed up the testing of samples if two wheels were available, one with a coarser grit and one with the fine, final polishing grit. Also by having students also work on the project, one will not be delayed in preparing samples by having to wait for the someone else to finish with the only polishing wheel.

Item #3: Laser Light

Success has been achieved by using electrochemical methods to encourage

weaker chemical etchants to produce more meaningful patterns on semiconductor crystals. Another method to improve etching is to enhance the process photochemically. Longwood College already has an ultraviolet lamp that emits UV light that will be used to test photochemical etching methods, but this may be too weak to produce sufficient intensity. An arc lamp is also available at Longwood College. A laser light is needed to provide radiation of sufficient intensity to activate the photochemical etches.

3. Schedule:

Jan-Apr 1996:

- ▶ Literature search to find and catalog existing etchants and procedures.
- Thermodynamic analyses of known and potential semiconductor etches.
- ▶ Order supplies for etchant testing and development.
- ▶ Design experiments to develop improved chemical and electrochemical and photochemical etchants.

May-Aug 1996:

- ▶ Prepare semiconductor crystals for analysis recording the positions and shapes of melt-solid interfaces in Bridgman furnaces.
- ▶ Test suitability of existing etchants for improved compositional analyses of semiconductor crystals.
- ▶ Continue to develop and test improved etchants and procedures. Update

Catalog of Etchants and analytical protocols.

- ▶ Enhance technology transfer and dissemination by presentations at NASA facilities and at crystal growth conferences.
- Presentation of results at ACCG-10.

Sep-Dec 1996:

- ▶ Complete data analysis, publications, and reports. Submit publication.
- ▶ Facilitate the transfer of technology to NASA centers.
- Prepare and submit final report.

ASA Grant
Proposed Budget
January 1996 - 31 December 1996

PERSONNEL:

P. Barber, 3 months, summer 1996 \$19,327
at Longwood College and/or NASA-LaRC

FDIC for P.Barber for 3 months \$1,479
(7.65% of salary)

SUBTOTAL, PRINCIPAL INVESTIGATOR \$20,805

Undergraduate Student Summer Research
(2 students @ \$6/hr, 40hr/wk, 10wk) \$4,800

FDIC for students \$367
(7.65% of salary)

SUBTOTAL, PERSONNEL \$25,973

INSTITUTIONAL OVERHEAD:

45.00% of total salaries & fringes \$11,688

SUBTOTAL: PERSONNEL & OVERHEAD \$37,660

PUBLICATION COSTS:

Preparation of Manuscripts and \$1,510
Conference Papers including
publication costs in J.Crystal Growth
and other journals.

Library, on-line literature search \$620

ASCCG, Amer.Conf.Crystal Growth
June 1996

air transportation \$685
ground transportation \$206
registration \$450
room {4days @ \$95/day} \$380
meals {4days @ \$35/day} \$128

SUBTOTAL, MEETINGS \$1,849

SUBTOTAL: PUBLICATIONS & PRESENTATION \$3,979

TRANSPORTATION:

To NASA-La RC
{4 trips @ \$340/wk} \$1,360

SUBTOTAL: TRANSPORTATION \$1,360

SUPPLIES:

Consumables: Paper, chemical, glass, \$1,600
Maintenance of Laboratory Equipment \$1,250
Upgrade of Software for NASA project \$2,305

SUBTOTAL: SUPPLIES \$5,155

EQUIPMENT:

Peristaltic Pump for etching \$1,990
Polisher/Grinder for semiconductor cr \$3,650
Laser lamp for etching \$2,335

SUBTOTAL: EQUIPMENT \$7,975

\$56,130

**TESTING AND FURTHER DEVELOPMENT OF IMPROVED
ETCHES AND ETCHING METHODS
FOR THE ANALYSIS OF BRIDGMAN GROWN
SEMICONDUCTOR CRYSTALS
WITH
AN EMPHASIS ON ONES SUITABLE FOR GROUND AND SPACE GROWN
LEAD TIN TELLURIDE**

**Patrick G. Barber
Professor of Chemistry
Longwood College, Farmville, Virginia 23909**

February 4, 1997

Abstract

Recent research by the faculty and undergraduate students at the chemical laboratories at Longwood College have applied chemical thermodynamics computer programs to the search and selection of potential new etches for compound semiconductors such as lead-tin-telluride, LTT. Two new chemical etches have been developed and tested. The first of the new etches uses silver(I) diammine, $\text{Ag}(\text{NH}_3)_2^+$, and the second one uses millimolar bromine/bromide, Br_2/Br^- . To provide quantitative data from the etching process a standard voltammetric analytical technique using a glassy carbon working electrode was adapted. This technique successfully identified the differences in etching depths and rates for LTT samples grown with and without magnetic damping. The proposed research project will continue the search for new etches using chemical thermodynamics, continue testing potential etches, and continue to improve techniques to quantify the etching process. The etches and techniques developed under this project will find immediate applications on both ground- and space-grown semiconductors such as LTT.

This project will address the need to assess the quality of semiconductor crystals and to correlate these properties with the experimental growth conditions. Emphasis will be given to improving *etches and etching techniques* that reveal the composition and crystal quality of doped semiconductors. Thermodynamic tables and calculations will be used to attempt to better understand the etching process and to aid in developing improved etches. Electrochemical methods will be further explored to find improvements in etching techniques.

Presentations to scientific forums such as the Eastern Regional Conference of the American Association for Crystal Growth, ACCGE/east-97, in September 1997, and *publications*

in scientific journals such as the *Journal of Crystal Growth* will be made to disseminate the technology developed under this grant. The developed analytical technology will be applied to improving furnace and ampoule designs, reducing experimental turnaround time, maximizing the benefits of each experimental run, and improving the quality and quantity of data available from experiments both on earth and in space.

1. Introduction:

1.1. Semiconductor Melt-Solid Interface:

The ability to produce semiconductor crystals of suitable composition and purity in preferred crystal growth orientations is essential for the commercial success of the modern electronics and communications industries. These materials are needed for defense equipment and for consumer products that are a significant part of the nation's economic health.

So important is this ability to produce these materials that they are being studied in the normal gravity of earth and in the microgravity of space. Experiments in crystal growth have flown on U.S. space missions in Spacelabs, Shuttle missions, and are being planned for Space Station. The Europeans have flown crystal growth experiments on sounding rocket flights such as the TEXUS project and on the D-1 mission on Space Shuttle. The Japanese also are involved in developing an extensive crystal growth experimental program for space. The Russian space effort also has placed a high priority on crystal growth experiments during manned flights and onboard the MPP Space Station.

As a part of another project, NASA developed the capability to visualize the melt-solid interface in real-time inside crystal growth furnaces such as those used in Bridgman growth of metals and semiconductors. Crystal growers can now interact with their experiments, and this has resulted in improved capabilities to record the melt-solid interface position and shape, to determine the actual crystal growth rate in situ, in real time, to better appreciate the thermal effects caused by furnace components such as thermocouples, to facilitate improved ampoule and furnace designs, and to provide remote sensing capabilities enabling scientists to conduct these

crystal growth experiments with a minimum of hands-on requirements. The technology now provides the ability to conduct crystal growth experiments efficiently in remote sites including the microgravity of space with scientists and engineers working in ground stations and requiring a minimum of astronaut time and attention. The improved crystal growth data already obtained in test systems using the elemental semiconductor germanium and the compound semiconductor lead tin telluride have proven the utility and value of this technology to the ground-based crystal growth community.

With all of this increased ability to adjust experimental growth conditions there is still the need to know how experimental conditions influence the quality of the resulting crystals. Improved methods to analyze the resulting crystals must still be developed, and this proposal will find methods to address these needs.

1.2. Development and Testing of Etchants

Because theories suggest that the crystal interface shape during growth affects the quality of the resulting crystal, there is a need to characterize more fully the products of semiconductor crystal growth in order to better understand the growth process itself, to better control experimental variables to improve the value and utility of the resulting products, and to facilitate the design of crystal growth furnaces and ampoules. This proposal seeks to improve the characterization of crystals by gathering chemical and electrochemical etchants reported in the literature, cataloging them, testing them, developing new or improved etchants and procedures where needed, and transferring this technology to the personnel at NASA Langley Research

Center. It further proposes to test the suitability of using spreading resistance probes to characterize the carrier and dopant levels in crystals. It will develop procedures for the use of these analytical technologies on Bridgman grown semiconductors such as LTT.

1.3 Report on the Development of Improved Crystal Analysis Technology:

To provide a summary of the development of this improved crystal analysis technology, reports to NASA Headquarters and other NASA centers such as LaRC and MSFC will be prepared. Analytical methods developed under this grant may find applicability to other compound semiconductors including HgCdTe.

1.4 Preparation of Journal Reports:

The significant technology developed to assess crystal quality will be disseminated through journal publications and presentations at scientific meetings. One presentation at the AACGE/east-97 meeting in September 1997 and one publication in the *Journal of Crystal Growth* are proposed for 1997.

2. **Justification of Budget Items:**

The budget for this proposal is attached, and a detailed description of the major items and how they relate to the work tasks is given below.

2.1. Personnel:

The salary for the principal investigator is included for two months during the summer of 1997. Part of this time will be spent at the NASA Langley Research Center in Hampton, Virginia, while the rest of the time will be spent at Longwood College in Farmville, Virginia. To prepare samples for analysis, actual crystal growth runs and image enhancements will be done at the Langley facility, since the needed equipment is already in place at that Center and it is not cost effective to duplicate this equipment at another site. The writing of the papers and reports is best done at the college. The gathering of existing etchant procedures, cataloging, testing, and developing improved etchants and etching procedures for observing variations in composition and structure are best done while working in the library and laboratories at Longwood College. The transfer of these improved techniques to the personnel at Langley must be done at NASA-LaRC.

Up to two undergraduate students will be employed on the project during the summer of 1997 and the academic year 1997-1998. Their participation in the project will greatly increase the number of experimental runs that can be made testing the new etches and techniques being developed. Their participation will also greatly enhance their educational experiences and will let them apply their knowledge and skills in a project with practical applications.

2.2. Publication Costs:

The necessary reports and journal publications must be typed and the presentation materials for the ACCGE/east-97 meetings must be prepared. Tables, graphs, and presentation viewgraphs and posters will need to be prepared. It is estimated that this will require

approximately eighty hours. Journal page charges for papers published by the *Journal of Crystal Growth* or a similar professional, peer-reviewed journal have been included.

2.3. Travel Costs:

To disseminate the results of this improved technology, the results are to be presented at two appropriate scientific meetings. It is proposed that this be done at the Eastern Regional Meeting of the American Conference of Crystal Growth to be held in New Jersey 28 September - 1 October 1997. This meeting is one of the principal meetings for American crystal growers. Presentation at this important meeting will facilitate the dissemination of this improved analytical technology and will facilitate cooperation in crystal growth projects. The estimated costs for registration, ground transportation, room and board are listed in the proposed budget.

Since some of the proposed work-tasks can only be completed using the facilities available at NASA Langley Research Center, the estimated expenses for travel to NASA-La are listed.

2.4. Supplies:

The costs for consumable paper, chemicals, glass, photographic film, cutting and polishing materials, and plastic supplies are shown on the proposed budget. Since the work tasks involve testing and development of improved etchants and electrochemical etching procedures, some chemicals and glassware are needed for the proposed project.

The equipment needed for the successful completion of this project has already been

purchased by Longwood College. There are some expenses associated with the maintenance of this equipment including microscope cleaning and servicing and supplies to maintain and use the optical, electrochemical, polishing, and computer equipment needed for this project.

The thermodynamic data bases and programs needed for this NASA project must be updated. The software used for the data analysis, microscope image analysis, and presentation quality figures and graphs also need to be updated. This enables not only the analysis of data but also the preparation of the viewgraphs, charts, figures, and images for the reports to NASA and the publications reporting on the results of this project.

2.5. Equipment: None requested.

4. **Schedule:**

Ongoing 1997-1998:

- ▶ Literature search to find and catalog existing etchants and procedures.
- ▶ Design experiments to develop improved chemical and electrochemical etchants.
- ▶ Assist in the transfer of etching technology to NASA research centers such as LaRC.

May-Aug 1997:

- ▶ Order supplies for etchant testing and development.
- ▶ Prepare semiconductor crystals for analysis recording the positions and shapes of melt-solid interfaces in Bridgman furnaces.
- ▶ Test suitability of existing etchants for improved compositional analyses of semiconductor

crystals.

- ▶ Continue to develop and test improved etchants and procedures. Update Catalog of Etchants and analytical protocols.
- ▶ Apply etches and techniques to ground-based semiconductors including LTT.
- ▶ Test spreading resistance measurements on Bridgman grown crystals and correlate the results of this analytical technique with results obtained from the chemical and electrochemical etching techniques.

Sep-Dec 1997:

- ▶ Apply etches and techniques to space-grown semiconductors including LTT.
- ▶ Enhance technology transfer and dissemination by presentations at national and international crystal growth conferences.
- ▶ Complete data analysis and correlation with semiconductor crystal quality.
- ▶ Prepare publication and presentation graphs, charts, and photographs.
- ▶ Prepare poster/talk and present results at ACCGE/east-97 conference.
- ▶ Facilitate the transfer of technology to NASA centers.

Jan-Apr 1998:

- ▶ Prepare and submit publication to *Journal of Crystal Growth* or other suitable professional, peer-reviewed journal.
- ▶ Prepare and submit reports on project to NASA.

NASA Grant
Proposed Budget
1 May 1997 - 30 April 1998

04-Feb-97
10:35:03

PERSONNEL

P. Barber, 2 months, summer 1997 at Longwood College and/or NASA-LaRC	\$12,889	58000
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FDIC for P.Barber for 2 months (7.65% of salary)	\$986	0.0765
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SUBTOTAL, PRINCIPAL INVESTIGATOR	\$13,875	
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Undergraduate Student Summer & Acad. Yr. Research (1 student @ \$6/hr, 5hr/wk, 30wk)	\$900	
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FDIC for students (7.65% of salary)	\$69	
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SUBTOTAL, PERSONNEL	\$14,844	
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INSTITUTIONAL OVERHEAD

45.00% of total salaries & fringes	\$6,680	0.45
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SUBTOTAL: PERSONNEL & OVERHEAD	\$21,524	
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PUBLICATION COSTS

Preparation of Manuscripts and Conference Papers including publication costs in J.Crystal Growth and other journals.	\$650	
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Library, on-line literature search	\$310	
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ACCGE/east-97, Amer.Conf.Crystal Growth
September 1997

air transportation	\$480	
ground transportation	\$85	
registration	\$350	
room {4days @ \$85/day}	\$340	
meals {4days @ \$35/day}	\$140	

SUBTOTAL, MEETINGS	\$1,395	
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SUBTOTAL: PUBLICATIONS & PRESENTATIONS	\$2,355	
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TRANSPORTATION:

To NASA-La RC
{4 trips @ \$220/wk} \$880

SUBTOTAL: TRANSPORTATION \$880

SUPPLIES:

Consumables:paper, chemical, glass, & plastic \$1,200
Maintenance of Laboratory Equipment \$950
Upgrade of Software for NASA projects \$2,100

SUBTOTAL: SUPPLIES \$4,250

EQUIPMENT:

none \$0

SUBTOTAL: EQUIPMENT \$0

TOTAL:

\$29,009

Estimating crystal quality in semiconductors using voltammetry

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Abstract

A voltammeter can be used to differentiate the crystalline quality of the compound semiconductor, lead-tin-telluride. A modified differential pulse stripping voltammetric analysis procedure is used with a millimolar bromine/bromide etchant. Higher quality crystals, which had been grown using a magnetically-damped Bridgman technique, required longer times for the onset of etching, had smaller rates of etching, and attained smaller depths of etching than did poorer quality crystals grown without magnetic dampening. This analysis procedure is faster, more amenable to quantitative results, and much safer than traditional etching techniques, which use highly corrosive chemicals. The results of the voltammetric analysis were verified using a standard Norr etch in a traditional electrochemical etching procedure and counting dislocation densities.

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{Classification Codes: Semiconductors, Lead-Tin-Telluride, Analysis, Magnetic Damping}

1 Introduction

The economic utility of compound semiconductor crystals depends upon the homogeneity of the crystal composition and the absence of defects. Traditionally, defects in crystals are detected by optical examination after selective etching of polished crystal surfaces. [1] This is made possible because the etching technique selectively removes material at dislocation sites and creates visible etch pits. [2] The dissolution of semiconductors depends upon the concentration of minority carriers near the cut and polished surfaces. The etching process often involves several steps including adsorption of one component of the etch onto the semiconductor surface, formation of oxidized products, adsorption of a second etchant component onto the oxidized products forming a soluble product, and finally desorption of the soluble product into the solution. [3] There are often optimum concentrations for etchant components manifested by the appearance of maxima in rates of etching. [4] Generally these chemical etchants are strong, corrosive or oxidative reagents having a concentration of one molar or greater. These strong chemical reagents sometimes leave films on the surfaces being etched. [5,6] Such opaque films obscure the surface features being sought. One method of reducing the formation of such surface films is to use very dilute etchant solutions, but to enhance the etching process with applied electrochemical voltages. [7] This enables the development of visible surface features at acceptable rates without the accompanying formation of surface films.

Compound semiconductors grown using the Bridgman technique generally do not grow as single crystals. To be analyzed, the crystals must first be cut. This is often not along a crystallographically low indexed face, and such cuts usually result in a random orientation. Consequently, searching for characteristic etch pit patterns on low index faces will not be successful.

A more rapid and reliable method was needed to assess the quality of the compound semiconductor lead-tin-telluride, LTT, which was grown with the Bridgman technique in the normal gravity of earth and which would be grown in the microgravity of space. Two procedures were developed.

2 *The lead-tin-telluride semiconductor crystals*

Four crystals of the compound semiconductor LTT were supplied by the NASA Langley Research Center for use as test samples. These crystals had been grown at the NASA Marshall Space Flight Center in Huntsville, Alabama, in Bridgman furnaces using the growth conditions summarized in table 1.

Table 1
LTT crystal growth conditions

sample i.d.	thermal gradient/ (K/cm)	growth rate/ (cm/hr)	magnetic field/ (gauss)
A	50	0.3	5
B	50	1.0	5
C	50	1.0	0
D	160	1.0	0

From the conditions of growth, crystal A, which was grown most slowly in the smallest thermal gradient and with the presence of a magnetic field, should have the highest quality, since magnetic damping reduces fluid flow in melts. Crystal D, which was grown most rapidly in the largest thermal gradient without the aid of a magnetic field, is expected to have the poorest quality and the greatest number of defects.

3 *Concentration dependent etch densities*

The standard Norr etch, which contains glycerol, potassium hydroxide, and ethanol in water [8], was used in an attempt to determine the relative quality of these four semiconductor crystals. The high concentrations in this etch reacted quickly and gave results that were equivalent with all four of the samples, and ordering the crystals was not possible as to their quality.

A new etch was developed using millimolar concentrations to discriminate among the four crystals. The etchant was diamminesilver (I) ion dissolved in ammoniacal ethanol. The

concentrations used were 12 mM silver nitrate, 1.25 M ammonium hydroxide, and 1.43 M denatured alcohol. After initially etching the surfaces of the four crystals and recording the results, the process was repeated increasing the concentration of silver ion until the final concentration of 80 mM was used. For each etching, the semiconductor crystal faces were polished using 0.05 μm alumina, placed in a platinum wire basket anode, submerged in the circulating etchant, and subjected to two volts for two minutes at room temperature. This electrochemical procedure removed material from the crystal surfaces, and the greater the number of dislocations present, the more easily the etching process occurred. When the results were compared for the extent of surface removed, it was possible to conclude that the quality of crystal A was better than B and that these were significantly better than crystals C and D. This ranking was as anticipated from the crystal growth conditions used but, although rapid, was not quantitative.

4 *Voltammetric analysis*

A standard electrochemical analytical method was adapted to follow the etching process quantitatively. [^{9,10}] An EG&G Princeton Applied Research Corporation Model 264A Polarographic Analyzer equipped with a Model 303A electrode using a glassy carbon working electrode was used in its differential pulse stripping mode. The electrochemical cell has three electrodes. The silver/silver chloride reference electrode is used to measure the voltage applied between it and the glassy carbon working electrode. The platinum auxiliary or counter electrode is used to measure the current flowing between it and the working electrode. In the differential pulse mode the first derivative of the current with respect to the applied voltage is recorded as a function of the voltage applied to the working electrode. The etchant in this cell also serves as the supporting electrolyte, and for this purpose a second etchant had to be developed. The supporting electrolyte/etchant used in the voltammetric analysis was a dilute aqueous solution of 4.9 mM bromine and 7.5 mM sodium bromide. In the stripping mode a constant voltage is applied for a short period of time, which in these experiments was 10 seconds. With the working carbon electrode held at -1000 mV, any metal cations, including any lead (II) ions produced from

dissolving the surface of the lead-tin-telluride crystal, will be drawn to and reduced to metal ions at the surface of the carbon working electrode. During the analysis phase, the voltage is increased from -1000 mV to -250 mV. Each metal atom adsorbed on the carbon electrode will be oxidized when its characteristic voltage is reached. In this analysis the lead oxidized at -610 mV in the bromine/bromide solution. The current measured depends upon the concentration of the lead(II) in the surrounding electrolyte, and this lead(II) ion concentration depends upon the ability of the etchant to ablate the surface of the semiconductor sample. This in turn depends upon the number and nature of dislocations on the surfaces of the semiconductor crystals. The analysis is a dynamic one that depends upon the establishment of a steady-state between the working electrode and the semiconductor sample. Figure 1 shows a sample of the data collected plotted as $\{di/dV\}$ in $\mu A/mV$ as a function of the applied voltage in mV. Each scan is 30 seconds after the preceding one and is mechanically displaced vertically to separate each scan. The peak heights are proportional to the lead(II) ion concentrations in the supporting electrolyte. These peak heights can be converted into lead(II) ion concentrations in parts per million or $\mu g/ml$ by using a calibration curve prepared from lead(II) ion standards. The calibration curve is shown in figure 2.

5 Results

The results obtained from the voltammetric analysis can be plotted in terms of lead(II) ion concentration as a function of time. The results for the analysis of the four lead-tin-telluride crystals are summarized in figure 3. The graphs in this figure illustrate that the four semiconductor crystals differ as to the onset of etching, the rate of etching, and the ultimate extent or depth of etching. The same strength of etchant under the same conditions required much longer to initiate etching, the rate of etching was less, and the extent of surface removal was also significantly less for samples A and B than for C and D.

These results show that crystal A is higher quality than crystal B, and these two crystals are significantly better in quality than crystals C or D. This result is the same as obtained by the qualitative method of gradually increasing the etchant concentration using the ammoniacal silver

etchant, and the ordering of the crystals agrees with the quality expected from the crystal growth conditions.

The voltammetric method of analysis permits a rapid, quantitative analysis of the rate of surface removal, for this can be calculated from the slopes of the four curves in figure 3. The rate, R , in $\{\mu\text{g cm}^{-3} \text{s}^{-1}\}$ at which the lead is dissolved in the 10 ml sample cup from the semiconductor surface is measured by the voltammetric analysis. Dividing this rate by the atomic weight of lead gives the number of micromoles removed per second. Lead-tin-telluride crystallizes in a rock-salt, cubic unit cell having $a=6.460\text{\AA}$ and four lead atoms per cell. [1] Dividing the number of moles per second of lead by 4 gives the number of unit cells removed per second. Dividing by the exposed surface area, A , being etched gives the number of unit cells removed per second per square millimeter. Multiplying this result by Avogadro's number and adjusting the metric units gives the picometers s^{-1} of surface removed. Equation 1 summarizes this calculation, and table 2 summarizes both the data and the results of this analysis.

$$\begin{aligned} \text{Linear Etch Rate (pm/s)} = & R(\mu\text{g cm}^{-3} \text{s}^{-1}) (10 \text{ cm}^3) (6.02 \times 10^{23} \text{ mole}^{-1}) (10^6 \text{ mm}^2 \text{m}^{-2}) (10^{-6} \text{ g } \mu\text{g}^{-1}) \\ & * (6.460 \text{ \AA})^3 \text{ unit cell}^{-1} * (10^{12} \text{ pm m}^{-1}) * (10^{-10} \text{ m } \text{\AA}^{-1})^3 * (207.19 \text{ g} \\ & \text{mole}^{-1})^{-1} * (4 \text{ unit cell}^{-1})^{-1} * (A \text{ mm}^2)^{-1} \end{aligned}$$

[1]

$$\text{Linear Etch Rate (pm/s)} = (4.6925 \times 10^4) R/A$$

The results of this voltammetric analysis were compared with the more traditional method of etching and counting etch pit densities on the randomly oriented cut planes of the four semiconductor crystals. The crystals were electrochemically etched using a diluted Norr etch. The results, which are summarized in table 2, were consistent with the ordering of the crystals given in this experiment. The results obtained by the traditional optical methods of developing and then counting etch pit densities required longer times and are not amenable to automation.

Table 2

Summary of analysis data for the four LTT semiconductor crystals.

Sample	onset time min^{-1}	etch rate $\mu\text{g s}^{-1}$	concn limit $\mu\text{g cm}^{-3}$	crystal area mm^2	linear etch rate, pm s^{-1}	etch pit density, cm^{-2}
A	38	0.0055	2.5	136	1.9	0.14×10^6
B	18	0.010	3.3	293	1.6	0.46×10^6
C	9	0.027	6.2	168	7.5	0.59×10^6
D	6	0.013	5.2	130	4.7	0.94×10^6

The four LTT crystals were evaluated as to their quality using the results summarized in table 2. Normalizing to the values for crystal A in each case, the following rankings of the crystals were obtained:

Based on the etch pit density: $A = 3.3B = 4.2C = 6.7D$

Based on the linear etch rate: $A = 0.8B = 3.9C = 2.5D$

Based on the concentration plateau: $A = 1.3B = 2.5C = 2.1D$

Based on the onset of etching: $A = 2B = 4C = 6D$

The voltammetric method achieved a rapid analysis of the four semiconductor crystals and enabled them to be ranked according to their crystal quality. The analysis concluded that crystals A and B, which were grown with magnetic damping are about equal in quality and these two crystals are significantly better than C or D. Further analysis on additional crystals including those from other semiconductors is needed to better quantitatively correlate the results of the voltammetric analysis with specific crystal defects.

8 Conclusions

Two electrochemical etches using very dilute reagent concentrations were developed and used to evaluate the relative quality of four crystals of lead-tin-telluride grown in Bridgman furnaces. By using a modified, standard voltammetric analysis these crystals were evaluated and found to differ in the time for the onset of etching, the rate of surface removal, and the subsequent

extent of surface removal. The method enabled the small etch rates to be determined, and it facilitated the ranking of the crystals by quality.

Acknowledgments

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Stripping Voltammetric Analysis of
LTT Sample "D-2" in
Bromine/Bromide electrolyte

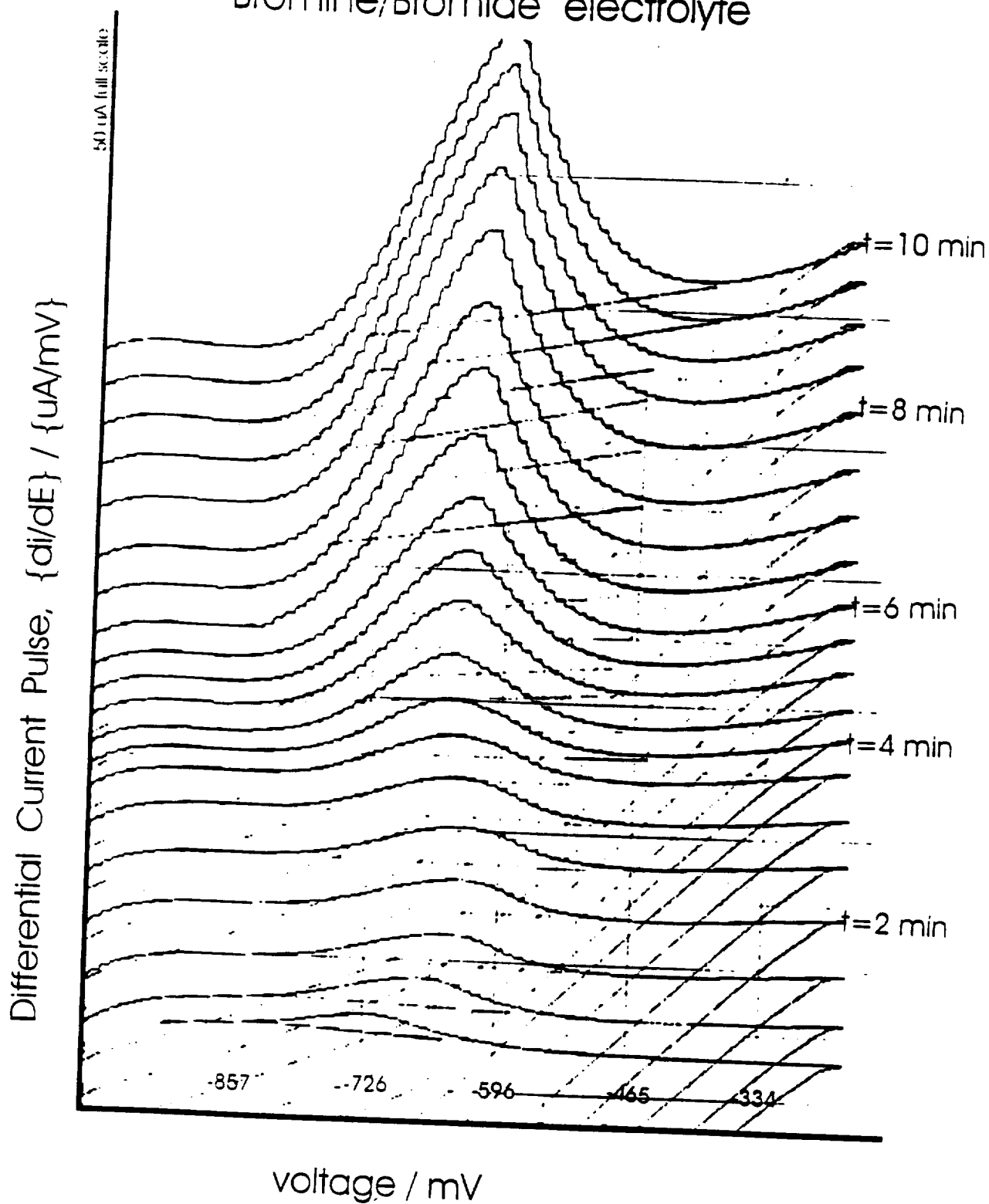


fig 1

Voltammetric Calibration of Pb(II)

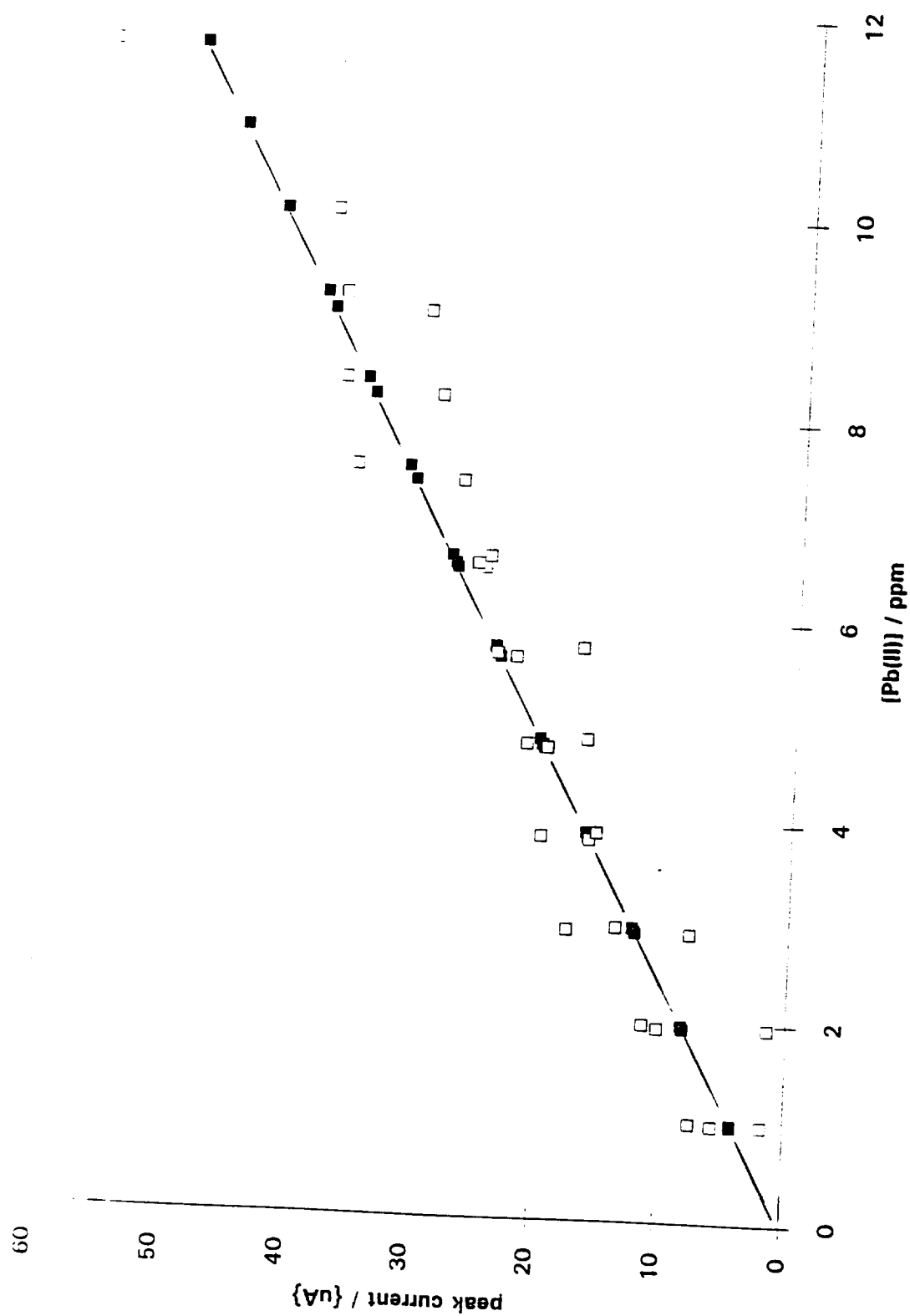


fig 2

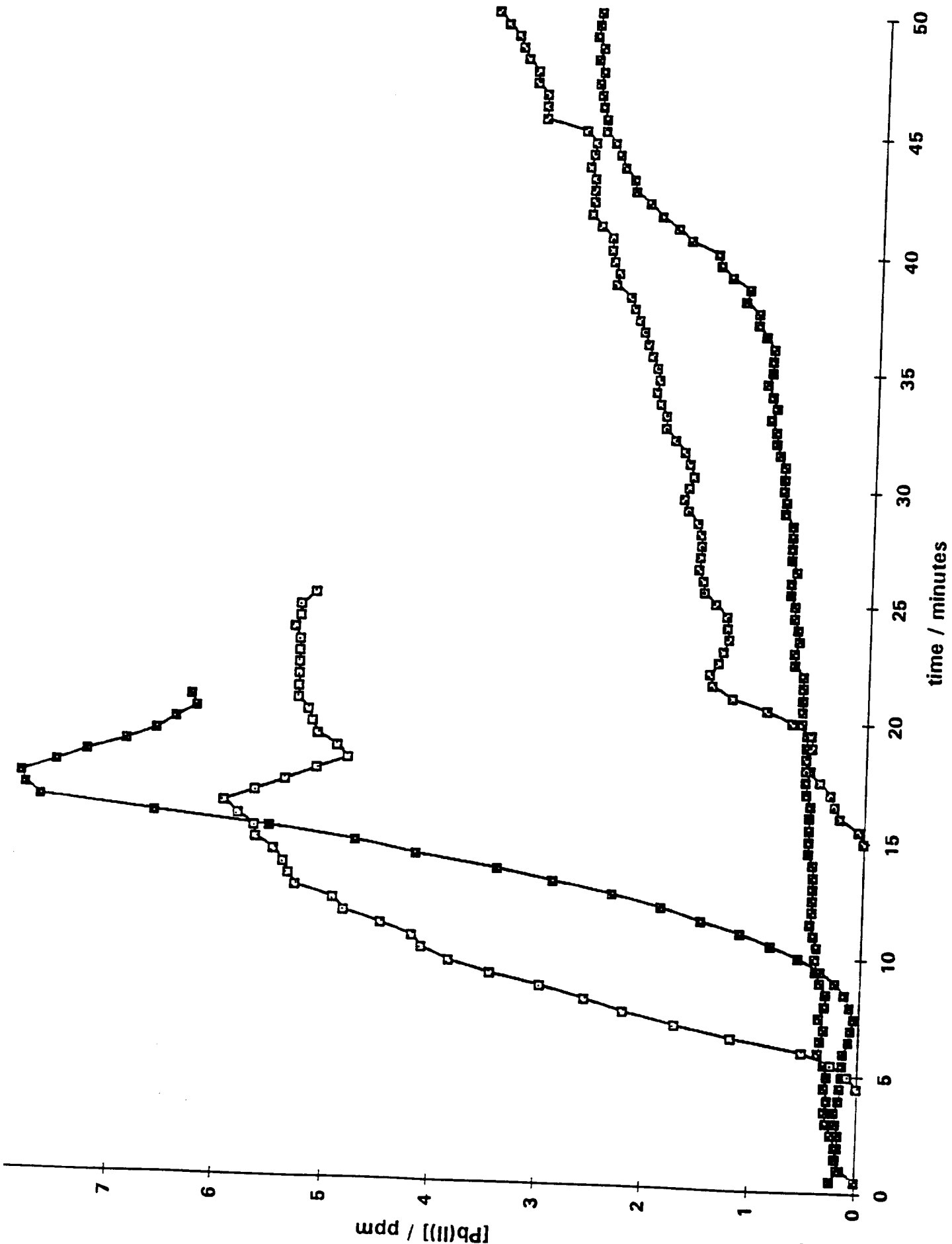
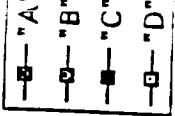


Fig 3

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